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A Product from the Photo-induced Reaction of Cholesterol in the Presence of Lead Tetraacetate and Iodine[1]

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Synopsis. The irradiation of a benzene solution of cholesterol in the presence of lead tetraacetate and iodine gives cholest-5-en-3β-yl *A*-homo-4-oxacholest-5-en-3α-yl ether in a 23% yield.

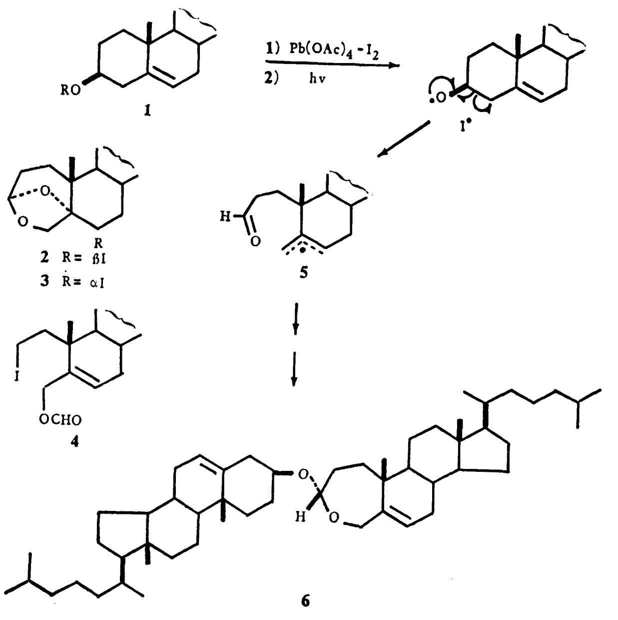
Earlier parts of this series have described the results of the investigations of the photo- and thermally-induced rearrangements of hypoiodites of cholesterol[2] and of the related 5-cholesten-3-ols[3] and *C*-nor-*D*-homosteroid-5-en-3β-ols[1] in the presence of mercury(II) oxide and iodine. Cholesterol (**1**) and epicholesterol hypoiodites in benzene have been found to give two oxabicyclic compounds, 3α,5-epoxy-6β-iodo-*A*-homo-4-oxa-5β-cholestane (**2**) and its 6α-isomer (**3**), accompanied by a moderate yield of 3-formyloxy-2-iodo-*A*-nor-2,3-seco-cholest-5-ene (**4**).[2] The introduction of methyl groups on the C-3 or C-4 of 5-cholestene framework has been found to result in appreciable variations in the products and their yields.[3] The pathways which explain the stereochemistry of the products and the effects of alkyl substitutions have been discussed in previous papers.[2,3]

The reaction involved a new type of ring enlargement. The active species generated from mercury(II) oxide and iodine was believed to be iodine oxide, I_2O,[4] which reacted with intermediary radical species to lead to the products. It is of interest to see, therefore, variations in the products caused by replacing mercury(II) oxide with other oxidizing reagents, *e.g.*, lead tetraacetate. The reaction of steroidal alcohols with lead tetraacetate and iodine reagent is also believed to proceed through hypoiodite or lead(IV) alkoxide.[5,6]

In this paper we will report on a considerable variation in the products in this reaction when the mercury(II) oxide and iodine reagents are replaced by lead tetraacetate and iodine.[5]

The irradiation of cholesterol in dry benzene containing a freshly prepared lead tetraacetate and iodine through Pyrex with a 100-W high pressure mercury arc under an argon atmosphere for 5 h gave a mixture of products. The examination of the products by TLC proved the absence of any oxabicyclic compounds, **2** and **3**, and formate, **4**. It showed, however, the formation of an appreciable amount of cholest-5-en-3β-yl *A*-homo-4-oxacholest-5-en-3α-yl ether (**6**), obtained from the thermally-induced reaction of cholesterol hypoiodite in the presence of mercury(II) oxide and iodine.[2] This ether, **6**, was isolated in a 23% yield as crystals by the aid of preparative TLC. A number of other unidentified products were also formed.

The variation in the products caused by lead tetraacetate is thus significant, but the role of the reagent which makes this difference is not certain, although the oxidation of intermediary radicals (*e.g.*, **5** in Scheme 1) to a cationic species with lead tetraacetate might play a part. A probable path *via* an allyl radical (**5**) has been suggested for the dimer **6**.[2] Since cholesterol is the steroid most abundantly available, and since **5** is readily hydrolyzed to *A*-homo-4-oxacholest-5-en-3α-ol and cholesterol with acid,[2] the reaction may be of use for the transformation of cholesterol into biologically useful compounds.



Scheme 1.

Experimental

For the instruments used and general procedures, see Ref. 2.

Irradiation of Cholesterol in Benzene Containing Lead Tetraacetate and Iodine. Cholesterol (300 mg) in benzene (44 ml) containing a freshly prepared lead tetraacetate (1.03 g) and iodine (600 mg) in a Pyrex vessel was irradiated with a 100-W high pressure mercury arc under an argon atmosphere for 5 h. The solution was then filtered, and the filtrate was washed with a sodium hydrogensulfite solution twice, a 10% sodium carbonate solution, and water successively and thereafter dried over anhydrous sodium sulfate. The evaporation of the solvent left a redidue which was subjected to preparative TLC with a mixture of 10 : 1 chloroform and acetone to give dimeric acetal, **6** (69 mg), together with a number of ill-defined products. The compound, **6**, was shown by a direct comparison to be identical with the specimen obtained from the thermal decomposition of cholesterol hypoiodite.[2]

References

1) Photo-induced Transformations. Part 59. Previous paper in this series: H. Suginome, K. Kato, and T. Masamune, *Bull. Chem. Soc. Jpn.*, **54**, 3042 (1981).

2) H. Suginome, A. Furusaki, K. Kato, N. Maeda, and F.

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Yonebayashi, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 236.

3) H. Suginome and N. Maeda, *Bull. Chem. Soc. Jpn.*, **53**, 2621, 2626 (1980).

4) M. Akhtar and S. Marsh, *J. Chem. Soc., C*, **1966**, 937; C. P. Forbes, A. Goosen, and H. A. H. Laue, *J. S. African Chem. Inst.* **25**, 144 (1972); C. P. Forbes, A. Goosen, and H. A. H. Laue, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 2346.

5) K. Heusler, J. Kalvoda, P. Wieland, G. Anner, and A. Wettstein, *Helv. Chim. Acta.*, **45**, 2575 (1962); J. Kalvoda, *J. Chem. Soc., Chem. Commun.*, **1970**, 1002.

6) For general reviews, see K. Heusler and J. Kalvoda, *Angew. Chem.*, **76**, 518 (1964); J. Kalvoda and K. Heusler, *Synthesis*, **1971**, 501.